

1917

P93



VACUUM DISTILLATION OF ZINC

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

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COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1917



2.6.2018 Thursday

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May 29 1917

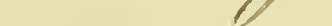
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## VACUUM DISTILLATION OF ZINC

I

## INTRODUCTION

The electrolytic refining of impure zinc, using sheets of zinc as the cathode and plates of the impure zinc to be refined as the anode, is analogous to the electrolytic refining of impure copper, but, simple as the method appears from the theoretical standpoint, it is attended by numerous practical difficulties, which are so serious that the process has not yet proved applicable on a large scale, notwithstanding the unquestionable usefulness which it would have for the refining of zinc contaminated with lead and other impurities.

Electrolytic refining of impure zinc has so far failed to be economically successful, chiefly because of the difficulties involved in the removal of the impurities and the great care and skilled labor required in the production of a deposit of zinc that can be rolled. The result of experience is that although impure zinc can be refined electrolytically, up to the present time it has not proved commercially successful to do so, except in the case of the impure zinc crusts obtained from the desilverization of lead, which is a special process of comparatively little importance in the metallurgy of zinc proper.

Notwithstanding the simplicity of the distillation process of zinc in theory its practical execution is attended by so many inherent difficulties that developments along the lines that have been followed in the metallurgy of lead and copper, especially the introduction of furnaces of large capacity and



labor saving appliances, have been impossible, and consequently the metallurgy of zinc remains today essentially the same as in the beginning. Chief among these difficulties is the ease with which zinc vapor can be oxidized by carbonic dioxide and the necessity of producing a gas of high zinc content.

With the above mentioned facts in mind the following work was undertaken to develop a process of making pure zinc, electrolytically. Before describing the process developed two important experimental facts should be mentioned:

1. Zinc alloys with copper to form brass without an appreciable increase of volume due to displacement.

2. Zinc can be distilled from brass in a vacuum at a reasonably low temperature at about  $375^{\circ}\text{C}$  to  $400^{\circ}\text{C}$ . These two processes will now be separately considered.

1. Diffusion of zinc into copper.

The process of diffusion of copper into zinc can be easily shown by immersing a rod of copper for a short time in molten zinc. An adherent coating is formed, consisting of a brittle silvery-white alloy rich in zinc. A section cut through the rod shows that within this layer of a yellow alloy, the B. solid solution, which appears, under low magnification, to be separated from the unaltered copper of the interior of the rod by a sharp boundary. If the rod is now heated for several hours at a temperature of about  $700^{\circ}$ , and then slowly cooled, diffusion is found to have occurred when the specimen is again examined, zinc diffusing inward from regions of high to those of low concentration, that is, from the outer zone to the inner zone. In the course of diffusion, the copper is no doubt replaced molecule by molecule





by a solid solution containing a compound probably  $\text{Cu}_2\text{Zn}$ <sup>1</sup>. The formation of a solid solution must be a necessary condition of true diffusion in an alloy. The change of volume due to the replacement is comparatively small, so that cracking does not take place until a thick layer of the alloy has been formed.<sup>2</sup>

### 3. Separation of Zinc from Copper by Distillation.

Considerable attention has been devoted in recent years to the behaviour of metals and alloys when heated in a vacuum, the object being to obtain a separation of the metal or metals at a lower temperature than usual, and to prevent loss by oxidation. Recent patents indicate that such processes have been proposed, and to some extent adopted in various countries and for different purposes.<sup>3</sup>

While there is no available evidence at present that any of the above processes has obtained a commercial success, there is good reason to anticipate that with improved methods of producing and maintaining a vacuum, and with a better system of applying heat, metallurgical processes of far reaching importance may ultimately be obtained.

In a paper by Groves & Turner some experiments were conducted in a vacuum furnace<sup>4</sup> and it was shown that when brass is heated in a vacuum to the melting point of copper, the zinc is quantitatively removed and the copper left behind in the metallic state. Similarly, if an alloy containing zinc and iron is heated in a vacuum, the two metals can be readily and completely separated, provided a proper temperature is employed. Below about  $500^\circ$  the separation is complete.<sup>5</sup>



In an experiment by Thomas Turner the approximate temperature at which zinc vapor begins to be evolved in vacuo was obtained by taking a hard glass tube and introducing into this some of the metal or alloy to be tested. The tube was then evacuated, until the pressure was less than that of 1 millimetre of mercury, and the tube was afterward sealed. It was then placed vertically in an air bath so arranged that the lower part of the tube, which contained the metal, could be heated to the desired temperature while the upper part of the tube was out of the air bath and kept well below the melting point of zinc. The air bath was then gradually heated until a deposit of zinc could be seen on the cool part of the tube. This deposit took place at a temperature of  $375^{\circ}$  to  $400^{\circ}$  C.





## PRELIMINARY EXPERIMENTS

The method first attempted for combining these two experimental facts, first, that zinc will diffuse into copper forming brass, and second, that zinc will distill from brass in a high vacuum at a temperature of about  $400^{\circ}\text{C}$ , consisted of electrolyzing some zinc salt, the chloride preferred, using a hollow evacuated copper cathode. In this way the zinc first alloys with the copper, then diffuses through the latter and distills off into the vacuum from the inside of the tube. The advantages hoped for by such an arrangement are as follows:

1. The production of a very pure grade of zinc ~~inasmuch~~ ~~that~~ the bath will not be occluded.
2. Continuous operation.
3. The prevention of loss of efficiency by formation of metallic fog in bath.
4. The prevention of loss of zinc by oxidation and volatilization.
5. Higher current efficiency by elimination of side reactions.
6. A possibility of thus preparing other metals, such as calcium, strontium, barium, and magnesium, that have not previously been obtained pure.

In order to ascertain the possibility of electrolyzing zinc chloride and making the zinc alloy with a copper cathode, the following experiment was performed. A chloride bath consisting of 80 parts of zinc chloride and 20 parts of sodium chloride



was electrolyzed in a 1/16" copper walled dish. This was heated with a gas flame, the temperature being measured by a Haskins thermocouple. When the bath was at a temperature of 350° C electrolysis was started with a current of one ampere and a voltage of 4. After three hours the zinc had diffused through the wall of the dish giving a yellow-red color to the outside surface.

The apparatus next constructed consisted of a false bottom copper cup cathode 1/16" in thickness, being made by welding together the edges of two copper cups placed one within the other. The welding was done with phosphor copper alloy, using a borax flux. This construction left a space between the walls of the cups which could be evacuated. However, this type of vacuum cathode offered many unforeseen difficulties. The copper weld was found on standing to develop minute pin-hole leaks. A glass tube was to be used to collect the zinc vapor, but it was found impossible to seal the glass to the copper tube and have the joint hold a vacuum very long at the temperature of operation. Cements and glasses of many kinds were used but none was found satisfactory. On account of these difficulties in the way the copper cup cathode was ~~disbanded~~ <sup>disassembled</sup> and a new design adopted.





## FINAL EXPERIMENTS AND RESULTS.

1. Construction of Furnace.

The furnace used was constructed as follows: A fire-clay crucible (a), 6" high and 4" in diameter was wound with 50 feet of #18 nichrome wire, the terminals being fastened to binding posts imbedded in fire clay (B). The crucible was now placed in a can container (C) and packed with Kieselguhr. In the inside of this crucible was placed the copper spiral (D) serving as a vacuum cathode, which extended through the bottom into an iron plug (E) (construction of D and E described later). The anode was made from a carbon rod which had a channel in it to carry off the chlorine liberated during electrolysis. The 1" iron plug (E) was screwed into an iron pipe 14" long (F). The pipe was wound with 30 feet of #18 nichrome wire for the first 7" and a hard glass tube was placed inside to furnish a clean surface for the zinc to condense on. The outer end of the pipe was cooled by a copper coil carrying water.

2. Construction of copper vacuum cathode.

The vacuum cathode was made from a 3 foot piece of copper tubing, 5/16" in diameter. This was first annealed and then filled with sand, closing both ends of the tube when filled by hammering. The tube was now twisted into a cone shaped spiral. After pouring the sand out, one end of the tube was electroplated until air-tight.

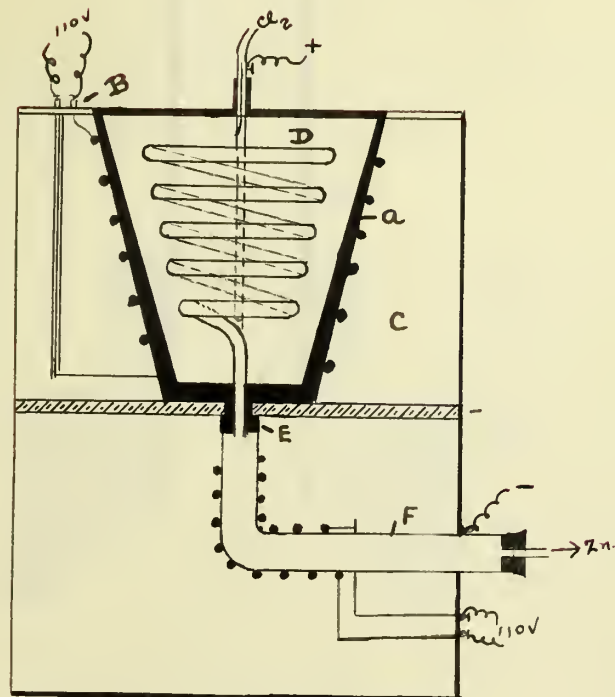
3. Construction of copper-iron joint.

A 1" iron plug (A) (sketch 3) was drilled with a 5/16" hole. The copper tubing was pushed through this and forced against the sides of the iron plug (B) by driving a cone shaped tool into it.



# Cross Section of Furnace

Scale 1"  $\frac{3}{8}$ "

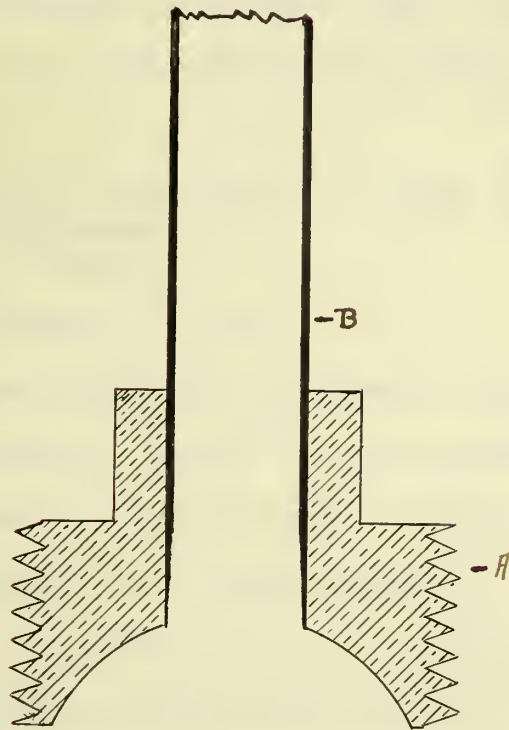






# Copper-Iron Joint.

Scale 1" = 2"





This joint was now tested for leaks at room temperature and found vacuum tight. Since copper expands faster than iron, it is obvious that this design of joint becomes tighter as the temperature is increased.

#### 4. Results.

(A) Electrolysed a mixture of 4 parts zinc chloride and one part sodium chloride that had been previously fused to remove as much moisture as possible.

Temperature at first  $400^{\circ}\text{C}$ . Later heated to about  $450^{\circ}\text{C}$ .

Time - 5 1/2 hours.

Current - 4.5 amp.

Volts - 4.

Press. of mercury - 3 mm.

Zinc tested for copper and iron by potassium ferro-cyanide showed these metals to be absent. Weight of zinc produced, 4 grams, most of the metal separated by electrolysis in this first run being left behind in alloy with the copper cathode. There was also some loss of zinc by oxidation, due to a leak at the end of the run. The copper cathode in this case was of a uniform brassy color without any surface separation of zinc. Current density at first .01 ampere per sq. cm., afterwards increased to .02 ampere per sq. cm.

(B) Electrolysed mixture left over from the first run with an addition of electrolyte to make up for loss.

Temperature -  $320^{\circ}\text{C}$ .

Current - 4.5 amp.

Volts - 3.

Press. of mercury - 3 mm.

Time - 12 hours.

A metallic glaze was found on glass, no dense deposit of zinc as in (A) found. Temperature was apparently too low and all the deposit remained in the iron plug and the copper tube. The upper



part of the cathode at the end of this run was covered with a deposit of spongy zinc, showing that the temperature was too low to permit the rapid alloying of the zinc with the copper, or else that the current density was too high for this temperature.

Current density .032 ampere per sq. cm.





## CONCLUSION

The following facts can be concluded from the results obtained:

1. It is possible to electrolyze a zinc chloride bath, making the zinc alloy with a copper cathode, and have the zinc distill off from the inside of this cathode under diminished pressure.
2. An electric furnace has been designed and constructed for this purpose.
3. Zinc free from copper and iron can be made in this way.
4. Copper vacuum cathode should at least be 2" under surface of electrolyte so as to prevent corrosion and to keep it at the temperature of bath.
5. The deposition of zinc should not take place too rapidly. A current density of about .02 ampere per sq. cm. appears to be about the maximum possible to use at the minimum temperature for the distillation of the zinc from the copper cathode.





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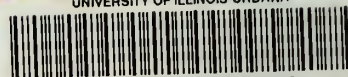


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